D.2 Technical Memorandum RE: Sensitivity and Uncertainty Analysis of Workplace Air Concentration Models Used in the PWB Exposure Assessment

TECHNICAL MEMORANDUM

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PWB Project File (Project # X823-941)

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RE: **SENSITIVITY AND UNCERTAINTY ANALYSIS OF WORKPLACE AIR CONCENTRATION MODELS USED IN THE PWB EXPOSURE ASSESSMENT**

I. INTRODUCTION

This technical memorandum is submitted to the RM2 Work Group for review and comment. Sensitivity and uncertainty analyses of the fate and transport models used in predicting workplace air concentrations of MHC chemicals were performed. (These air concentrations are used in the exposure assessment to estimate worker inhalation exposures.) The model parameters having the greatest effect on chemical air concentrations in the workplace are identified. A quantitative uncertainty analysis was also performed. These analyses serve to pinpoint and validate key parameter assumptions.

II. METHODS AND RESULTS

Sensitivity Analysis

The first step in this analysis was to determine the parameters in the air transport models that had the largest impact on the workplace chemical air concentrations regardless of parameter variability. This was done by independently varying each parameter in the model by a specific amount and observing the effect on chemical air concentration. This allows a comparison to be made between parameter importance in terms of model sensitivity because their effects on chemical air concentration were obtained independently of the other parameters.

Table 1 lists the parameters that had the greatest effect on workplace air concentration. Small changes in some parameters caused the model results to vary widely, indicating a need to determine the uncertainty associated with these variables. For sparged baths the example chemical was formaldehyde, and fluoboric acid was used for the unsparged bath analysis. Other chemicals were observed in the sensitivity analysis to learn whether the effects per chemical would vary with these parameters. This means that every chemical will not be affected in exactly the same way when varying parameters, but will exhibit close behavior. This initial sensitivity analysis was used primarily to select the important parameters for the Monte Carlo Analysis to follow, and as a check for that analysis.

Table 1. Model Sensitivity to Parameters

Parameters (x)	Δ x [1] (%)	Effects on Sparged Volatiles[2] (%)	Effects on Sparged Non-Volatiles[3] (%)	Effects on Un-Sparged Volatiles[4] (%)
Enthalpy (Aqueous or Gas)	10	-23.6	NA	-4.4
Bath Temperature	10	16.2	4.8	19.3
Henry's Law Constant (H_C)	10	10.0	NA	10.0
Bath Concentration of Chemical	10	10.0	10.0	10.0
Process Room Volume	10	-9.1	-9.1	-9.1
Air Turnover Rate	10	-9.1	-9.1	-9.1
Bath Surface Area	10	5.9	2.3	7.4
Air Sparging Rate	10	2.1	7.7	NA
Air Velocity Across Tank Surface	10	3.7	1.2	4.9
Molecular Weight	10	-2.0	NA	-2.1

1: Percentage increase in each parameter that produces corresponding percentage change in chemical room air concentration as shown in columns 2, 3, and 4.
2: Percentage increase or decrease in room air concentration of air-sparged volatiles due to parameter variation (Δ x) of 10 percent.
3: Percent increase or decrease in room air concentration of air-sparged nonvolatile (i.e., vapor pressure < $1x10^{-3}$ torr) due to parameter variation (Δ x) of 10 percent.
4: Percent increase or decrease in room air concentration of unsparged volatiles due to parameter variation (Δ x) of 10 percent.

For example, a 10% increase in bath surface area increases a sparged volatiles' workplace air concentration by 5.9%, while only increasing a sparged non-volatile or salt air concentration by 2.3%. Each parameter listed was also increased by 20% to determine if its relationship to air concentration was highly nonlinear, but none exhibited a significant trend in this area. Parameters not listed in Table 1 exhibited negligible effects on the model (<0.001 percent change in air concentration). These negligible parameters are:

- Bath volume;
- Surface tension coefficients;
- Molecular volume;
- Water densities and viscosities (due to variation of temperature in baths);
- Sparged bubble diameter; and
- Correction factors in the Berglund and Lindh model (see Exposure Assessment Draft, 1996).

Monte Carlo Analysis

Overview and Approach. After evaluating the sensitivity of the model to each parameter the next step was to examine model sensitivity and uncertainty using Monte Carlo Analysis. This was done with a Monte Carlo software package (Crystal Ball, Decisioneering, Inc.) in conjunction with a spreadsheet program (Lotus 1-2-3). The air transport equations outlined in the Exposure Assessment Draft (May 15, 1996) were used with the distributions for each parameter from the Workplace Practices Survey to perform this Monte Carlo Analysis.

Many different methods are available to propagate parameter distributions through a model and analyze the results. However, the difficult task of correlating complex nonlinear models and their parameters with some kind of regression algorithm severely limits the available techniques. The Latin Hypercube modification of the Monte Carlo method is agreed upon by many researchers to be the best way to perform a sensitivity/uncertainty analysis of contaminant transport models. In Latin Hypercube sampling, a probability distribution is divided into intervals of equal probability, thereby allowing for a more precise sampling routine because the entire probability range is more consistently represented (Decisioneering, Inc.). This probabilistic approach was used to generate a distribution of possible workplace air concentrations in contrast to a single point estimate.

Table 2 lists the assumptions used for the parameter distributions for the two bath type examples and describes the sources of information.

Crystal Ball was used to produce two independent Monte Carlo simulations, one for volatiles in air-sparged baths and one for unsparged baths. The number of iterations used for each simulation was 15,000. This was chosen to ensure adequate convergence and stabilization of the tails on output distributions (based on McKone and Bogen, 1991). The mass flux contribution from nonvolatiles in sparged baths is largely negligible and is not included to simplify the Monte Carlo simulations.

In addition to probability distributions, Crystal Ball calculates the percent contribution each parameter makes to overall model variance by computing Spearman rank correlation coefficients between every assumption and model result while the simulation is running. Spearman rank correlation coefficients differ from traditional linear regressions because ranks are assigned to observations and then substituted for the actual numerical values in the correlation formula. This correlation has distinct advantages over a simple linear regression. The relationship between variables is no longer assumed to be linear, and no assumptions of normality are made concerning the distributions of the variables as the relationship is nonparametric (Walpole and Myers, 1993). This parameter analysis combines model sensitivity and variable uncertainty.

Table 2. Parameter Assumptions Used in Monte Carlo Forecast

Parameters	Sparged Bath	Unsparged Bath	Source of Data
Process Room Volume	Lognormal Dist. based on survey data[a]	Lognormal Dist. based on survey data[b]	Workplace Practices Survey Data
Process Area Air Turnover Rate	Lognormal Dist. based on survey data[a]	Lognormal Dist. based on survey data[b]	Workplace Practices Survey Data
k (EPA, 1991) dimensionless mixing factor	Point estimate 1.0	Point estimate 1.0	Comments, G. Froiman /EPA RM2 Workgroup; June 16, 1996
Henry's Law Constant (H_C)	Normal Dist. based on avail. data[a]	Normal Dist. based on avail. data[b]	ORNL and other chemical info sources
Chemical Conc. in Bath	Triangular Dist.[a]	Triangular Dist.[b]	MSDS and Supplier info
Bath Surface Area	Lognormal Dist. based on survey data[a]	Lognormal Dist. based on survey data[b]	Workplace Practices Survey Data
Bath Temperature	Normal Dist. based on survey data[a]	Normal Dist. based on survey data[b]	Workplace Practices Survey Data
Bath Volume	Normal Dist. based on survey data[a]	Normal Dist. based on survey data[b]	Workplace Practices Survey Data
Air Sparging Rate	Point estimate 53.8 L/min	Point estimate 53.8 L/min	Midpoint of avail. values - chosen after model sensitivity seen to be small
Bubble Diameter	Lognormal Dist. based on avail. information[a]	Lognormal Dist. based on avail. information[b]	allowed to vary largely with little effect
Air Velocity across Bath Surface	Point estimate 0.508 m/s	Point estimate 0.508 m/s	recommended by EPA
Distance across pool Surface	Square root of bath area from survey data	Square root of bath area from survey data	directly correlated with area Dist.
Enthalpies, Gas and Aqueous States	Point estimate -35.9 kcal/mol & -27.7 kcal/mol	Point estimate -35.9 kcal/mol & -27.7 kcal/mol	ORNL and other chemical info sources
Activity Coeff.	Point estimate 1.45	Point estimate 25	ORNL and other chemical info sources
Surface Tension Coefficients	Point estimate 72, 21.92, &14.6 dynes/cm^2	Point estimate 72, 28.85, & 35 dynes/cm^2	ORNL and other chemical info sources

a: Attachment A shows these parameter distribution functions.
b: Attachment B shows these parameter distribution functions.

Results. Two types of results are presented: probability distributions for modeled air concentrations and the Spearman Rank Correlation results. The probabilistic chemical air concentration curves for each type of bath are presented in Figures 1 and 2. An uncertainty chart for each bath identifies the parameters that contribute most to model variance (Figures 3 and 4).

The parameter that contributes most to model variance for both bath types is air turnover rate in the process area. The range and standard deviation of reported air turnover rates from the Workplace Survey is very high. This causes it to contribute more to model variance than the process room volume. The variability of the room volume data is low and keeps it from even appearing on this list, despite the model being equally sensitive to changes in volume or turnover rate (as shown by Table 1). The chemical concentration in the bath is also high on the uncertainty charts because of the models' relative sensitivity to concentration and its variability.

Another important variable that appears on the sensitivity/uncertainty charts is bath temperature. This parameter is used to correct Henry's Law Constant (H_C) for temperature by an exponential relationship, but does not have much variability. H_C can also have a great effect on model outcome, depending upon the variability of the data. The distributions of H_C used here may not be entirely representative of the variation that can sometimes be encountered with this constant. For instance, Mackay (1991) has observed that a great deal of variation occurs with H_C when hydrophobic chemicals associate with the air-water interface and electrolytes or sorbents affect solubility in water. These variations are very difficult to characterize in a study unless H_C is measured under the conditions in question, which is not feasible here. Most chemical flux from sparged baths comes from the open surface volatilization equation (CEB, 1991), and will cause it to behave similarly to the unsparged bath equation as seen by results.

Comparison to Point Estimates. The probability distribution of formaldehyde air concentrations calculated by Monte Carlo Analysis were lower than expected from previously calculated point estimates. The 90th percentile from the frequency distribution is 0.61 mg/m^3, compared to 1.55 mg/m^3 calculated as a "high-end" point estimate (in the May, 1996, Exposure Assessment Draft). This suggests that the use of current point estimates results in a much more conservative air concentration than the 90th percentile. The point estimates in the exposure assessment use the 10th percentile air turnover rate, which controls air concentration because of its large variability shown in the uncertainty analysis.

A Monte Carlo distribution-based air turnover rate was determined using point estimates for all parameters and setting the air concentration equal to the 90th percentile probability frequency distribution from Crystal Ball. This was done for several chemicals in sparged and unsparged baths. This distribution-based air turnover rate was calculated as follows (from 3.3.1 in Exposure Assessment):

$$R_V = \frac{F_{Y,TOT}}{\mathrm{Conc} \cdot V_R \cdot k}$$

where:

Rv	= distribution-based air turnover rate (min^{-1})
Fy,tot	= total emissions from all air transport mechanisms (mg/min)
Vr	= room volume (m^3)
k	= dimensionless mixing factor (a default value of 1.0 was used)
Conc	= 90th percentile workplace air concentration from Monte Carlo Analysis (mg/m^3) determined using complete distributions for all parameters

This calculated air turnover rate was 0.0211 min^{-1} for formaldehyde in a sparged bath compared to the 10th percentile air turnover rate of 0.0083 min^{-1}. To ascertain the dependence of this distribution-based air turnover rate on chemical and bath type (sparged or unsparged) this calculation was repeated several times. These calculated (distribution-based) air turnover rates were:

- 0.0210 min^{-1} for copper chloride in a sparged bath; and
- 0.0206 min^{-1} for fluoboric acid in an unsparged bath.

Because air concentration estimates become more conservative as air turnover rates decrease, the value of 0.021 min^{-1} is recommended for estimating air concentrations for all chemicals to best approximate 90th percentile air concentrations with the available data.

The results of this sensitivity analysis are consistent with those obtained by Fehrenbacher and Hummel (1996). They suggest default air turnover rates of 14 m^3/min for a bounding, or maximum, estimate of exposure with this equation. The default input value of ventilation rate for obtaining "what-if", or average estimates is 85 m^3/min (this value lies in the central portion of the range for the parameter). An air turnover rate of 0.021 min^{-1} corresponds to a ventilation rate of 23 m^3/min, when combined with room volume.

IV. CONCLUSIONS

It is evident that a few parameters are key to modeling chemical flux from PWB tanks. These key parameters are:

- Air turnover rate;
- Bath temperature;
- Chemical concentration in bath; and
- Henry's Law Constant (H_C).

The air models' sensitivity to these parameters and their uncertainty provides a means of isolating them from less important variables. Isolating these variables allows for additional scrutiny to be placed upon the point estimate assumptions used for them in the volatilization models.

The air turnover rate assumption contributes most to overall model variance. The chemical bath concentration and bath temperature also contribute variance to the model, but are less important than air turnover rate. This statement is fortified by the fact that relatively accurate information is available on their distributions. H_C appears to be least important of the four, but may have more variability associated with it. The models appear to be largely indifferent to small changes in most other parameters.

A comparison of point estimates with the 90th percentile from Monte Carlo Analysis suggests that using the 10th percentile value for air turnover rate yields a point estimate that is highly conservative, and that an increased air turnover estimate of 0.021 min^{-1} would provide air concentration results closer to the 90th percentile.

V. REFERENCES

Decisioneering, Inc. 1993. *Crystal Ball Software*.

Fehrenbacher, M.C. and A.A. Hummel. 1996. "Evaluation of the Mass Balance Model Used by the Environmental Protection Agency for Estimating Inhalation Exposure to New Chemical Substances." *American Industrial Hygiene Association*, **57**:526-536.

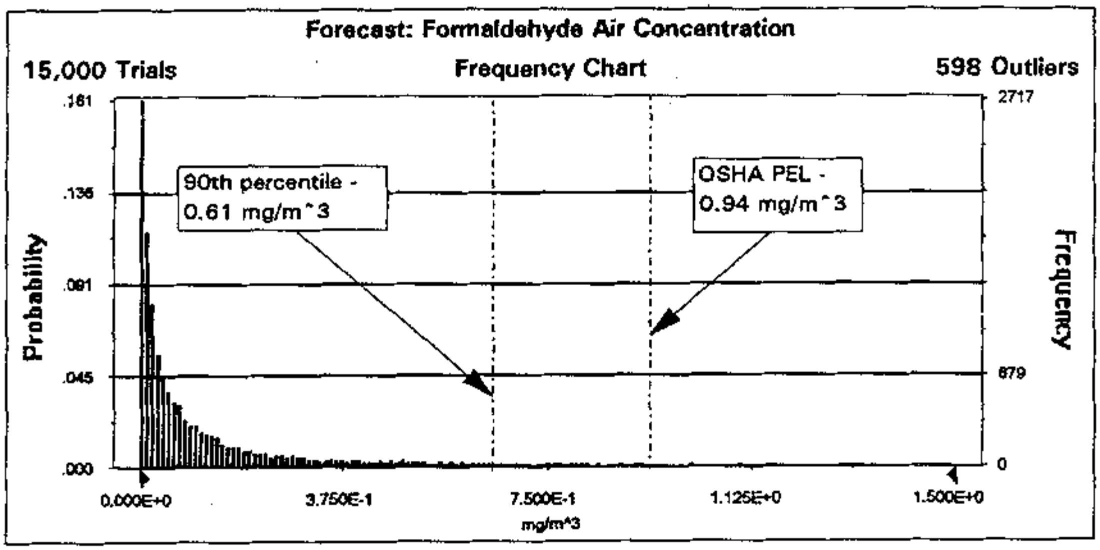
Mackay, D. 1991. *Multimedia Environmental Models: The Fugacity Approach*, Lewis Publishers, Inc.

McKone, T.E. and K.T. Bogen. 1991. "Predicting the Uncertainties in Risk Assessment: A California Groundwater Case Stud.," *Environmental Science & Technology*, **25**(10): 1674-1681.

U.S. Environmental Protection Agency. 1991. *Chemical Engineering Branch Manual for the Preparation of Engineering Assessments*. Washington, DC: U.S. EPA Office of Toxic Substances, February 28.

Walpole, R.E. and R.H. Myers. 1993. *Probability and Statistics for Engineers and Scientists*, New York: MacMillan Publishing Company.

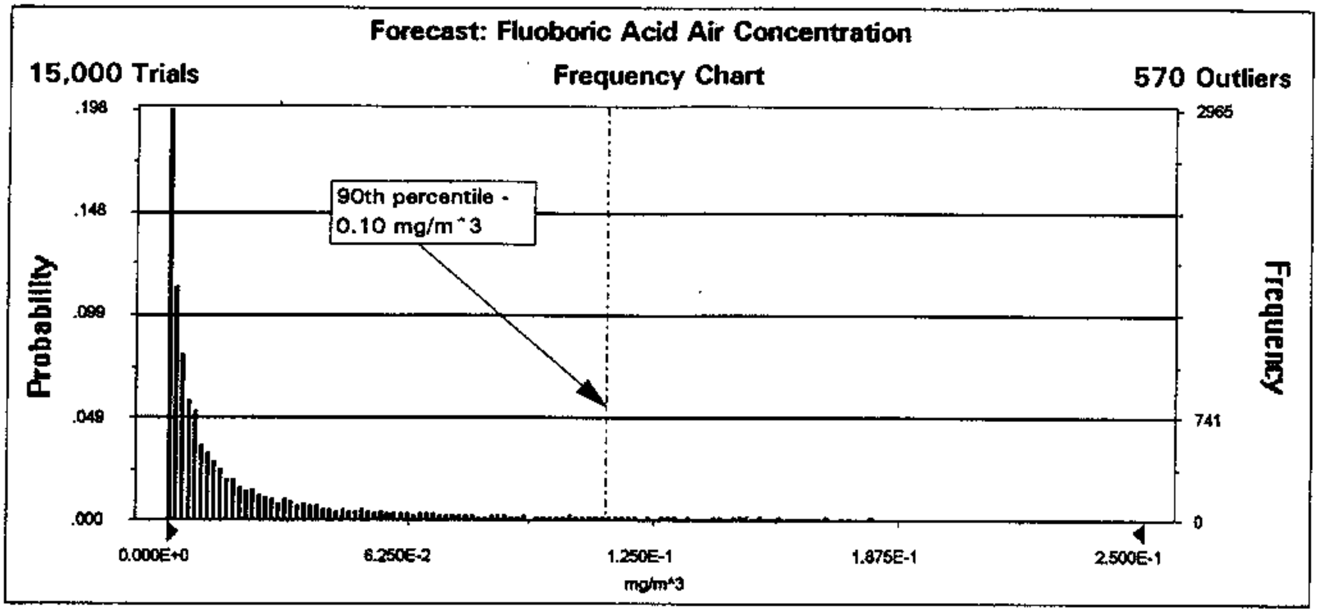
Figure 1.
Forecast Probability Distribution from Monte Carlo Analysis for Sparged Bath Chemical Workplace Air Concentration in mg/m^ 3 (Formaldehyde)



Percentiles:

Percentile	mg/m^3
0%	9.569E-05
10%	4.977E-03
20%	1.131E-02
30%	2.026E-02
40%	3.363E-02
50%	5.478E-02
60%	8.814E-02
70%	1.446E-01
80%	2.633E-01
90%	**6.107E-01**
100%	5.969E+01

Figure 2.
Forecast Probability Distribution from Monte Carlo Analysis for Unsparged Bath Chemical Workplace Air Concentration in mg/m^ 3 (Fluoroboric Acid)



Percentiles:

Percentile	mg/m^3
0%	1.600E-05
10%	7.568E-04
20%	1.689E-03
30%	3.146E-03
40%	5.288E-03
50%	8.389E-03
60%	1.368E-02
70%	2.294E-02
80%	4.206E-02
90%	1.004E-01
100%	1.265E+01

Figure 3.
Sensitivity Chart for Sparged Bath Chemical Parameters Spearman Rank Correlation

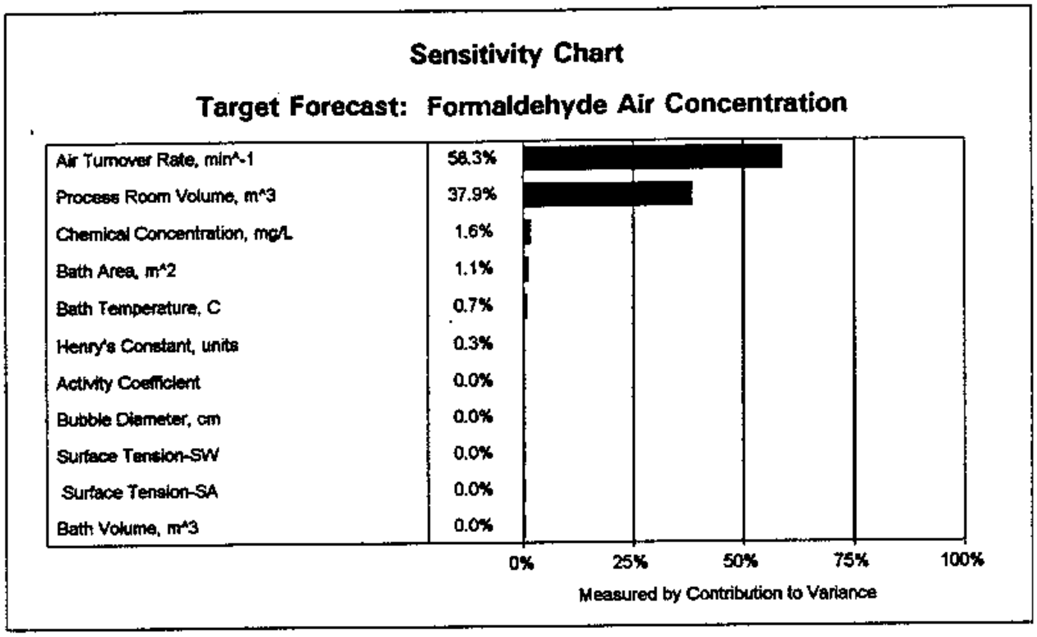


Figure 4.
Sensitivity Chart for Unsparged Bath Chemical Parameters Spearman Rank Correlation

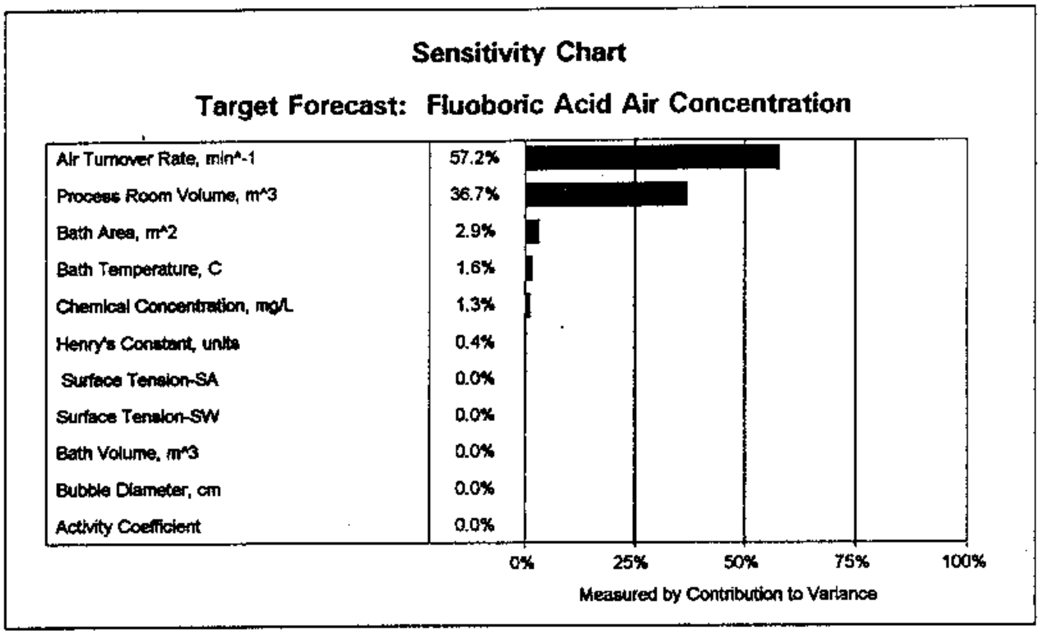
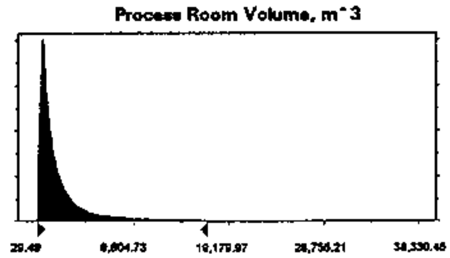


Figure 5.
Parameter Assumptions for Sparged Bath Monte Carlo Analysis - PDFs

Parameter: Process Room Volume, m^3
Lognormal distribution with parameters:

Geometric Mean	1,063.16
Geometric Std. Dev.	3.30

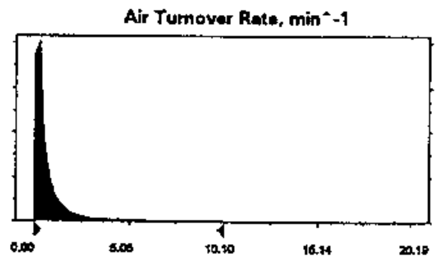
Selected range is from 33.00 to 17,000.00
Mean value in simulation was 1,911.23



Parameter: Air Turnover Rate, min^-1
Lognormal distribution with parameters:

Mean	0.74
Standard Dev.	2.00

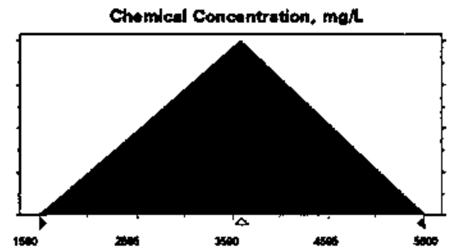
Selected range is from 0.00 to 10.10
Mean value in simulation was 0.64



Parameter: Chemical Concentration in Bath, mg/L
Triangular distribution with parameters:

Minimum	1580
Likeliest	3680
Maximum	5600

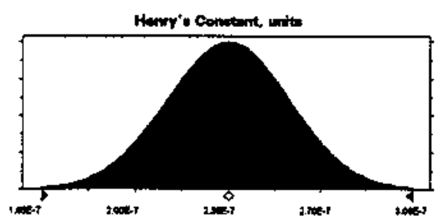
Selected range is from 1580 to 5600
Mean value in simulation was 3620



Parameter: Henry's Constant, atm*m^3/mol
Normal distribution with parameters:

Mean	2.35E-07
Standard Dev.	2.35E-08

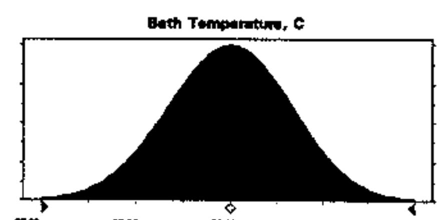
Selected range is from -Infinity to +Infinity
Mean value in simulation was 2.35E-7



Parameter: Bath Temperature, degrees C
Normal distribution with parameters:

Mean	38.89
Standard Dev.	3.89

Selected range is from 20.00 to 58.00
Mean value in simulation was 38.89



Parameter: Bath Surface Area, m^2
Lognormal distribution with parameters:

Log Mean	-0.11
Log Std. Dev.	0.33

Selected range is from 0.00 to 3.72
Mean value in simulation was 0.94

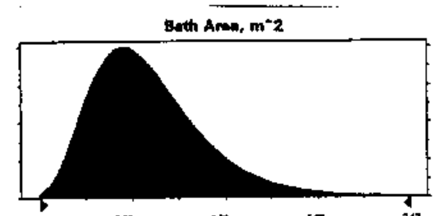


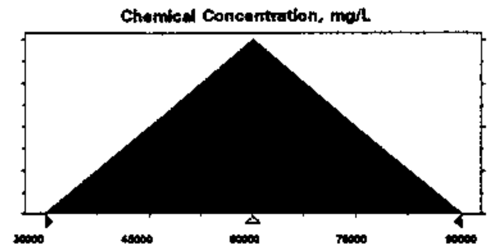
Figure 6.
Parameter Assumptions for Unsparged Bath Monte Carlo Analysis - PDFs

Parameter: Chemical Concentration in Bath, mg/L

Triangular distribution with parameters:

Minimum	30000
Likeliest	60000
Maximum	90000

Selected range is from 30000 to 90000
Mean value in simulation was 60000

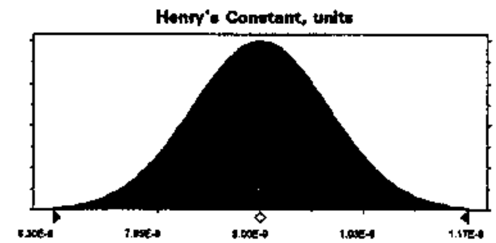


Parameter: Henry's Constant, atm*m^3/mol

Normal distribution with parameters:

Mean	9.00E-09
Standard Dev.	9.00E-10

Selected range is from 5.40E-9 to 1.26E-8
Mean value in simulation was 9.00E-9

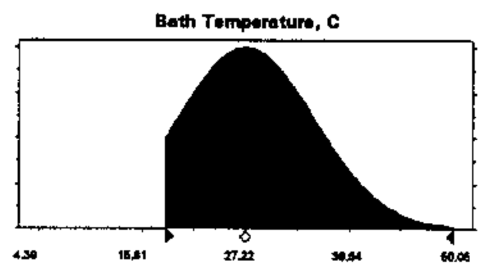


Parameter: Bath Temperature, degrees C

Normal distribution with parameters:

Mean	27.22
Standard Dev.	7.61

Selected range is from 18.39 to 50.39
Mean value in simulation was 28.95

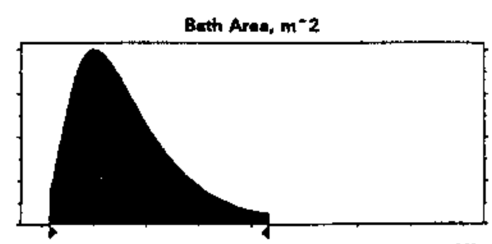


Parameter: Bath Surface Area, m^2

Lognormal distribution with parameters:

Geometric Mean	0.49
Geometric Std. Dev.	1.67

Selected range is from 0.15 to 1.28
Mean value in simulation was 0.53



Note: Process room volume and process room air turnover rate assumptions are the same as for formaldehyde (Figure 5).